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TITLE: Printable material

## Abstract Paragraph (1):

A printable material which includes a flexible first layer having first and second surfaces and a second layer. The first layer may be a film or a cellulosic nonwoven web. The second layer overlays and is bonded to the first surface of the first layer and includes a nonwoven web. The first layer has a basis weight of from about 20 to about 140 grams per square meter. The thermoplastic polymer has a melting point of from about 90.degree. C. to about 250.degree. C. and the second layer has a basis weight of at least about 10 grams per square meter. The first layer may be a cellulosic nonwoven web, such as a latex-impregnated paper. The second layer may be thermally bonded to the first layer or bonded by an adhesive. A release layer may be present between the first layer and the heat-activated adhesive. The second layer may contain from about 0.1 to about 20 percent by weight, based on the weight of the second layer, of a material which increases the viscosity of an ink jet ink when printed on the second layer. The second layer also may contain from about 0.1 to about 5 percent by weight, based on the weight of the second layer, of a cationic polymer. When the second layer is prepared from a thermoplastic polymer, the ink jet printable material may be used as a heat transfer material. Methods of preparing the printable material also are described.

#### Summary of Invention Paragraph (2):

[0001] The present invention relates to a printable material, such as an <u>ink jet</u> printable material. In certain embodiments, the present invention relates to a heat transfer material.

#### Summary of Invention Paragraph (3):

[0002] The popularity in recent years of personal computers in homes and businesses has stimulated the development of several types of printers. The earlier, relatively low cost printers were impact or dot-matrix printers which utilized a ribbon and a plurality of pins to place a desired image on a substrate which typically was paper. While the better dot-matrix printers are capable of near letter-quality printing, they typically are both slow and noisy. Laser printers are quiet, produce high-quality images, and can print an excess of four pages per minute. Such printers, however, tend to be too expensive for common use in homes and even in some smaller businesses; this is especially true for color laser printers. Ink jet printers fill the gap between dot-matrix printers and laser printers, both with respect to cost and image quality.

## Summary of Invention Paragraph (4):

[0003] The advent of improved, relatively low cost color printers has aided the development of a significant industry which involves the application of customer-selected designs, messages, illustrations, and the like (referred to collectively hereinafter as "customer-selected graphics") on articles of clothing, such as T-shirts, sweat shirts, and the like. These customer-selected graphics typically are commercially available products tailored for that specific end-use and are printed on a release or transfer paper. They are applied to the article of clothing by means of heat and pressure, after which the release or transfer paper is removed.

### Summary of Invention Paragraph (5):

[0004] Some effort has been directed to allowing customers the opportunity to prepare their own graphics for application to an article of clothing. The preparation of such graphics may involve the use of colored crayons made from a heat-transferable material. Such crayons have been made available in kit form, which also includes an

unspecified heat <u>transfer</u> sheet having an outlined pattern thereon. In a variation of the kit, the transferable pattern is created from a manifold of a heat <u>transfer</u> sheet and a reverse or lift-type copy sheet having a pressure transferable coating of heat transferable material thereon. By generating the pattern or artwork on the obverse face of the <u>transfer</u> sheet with the pressure of a drafting instrument, a heat transferable mirror image pattern is created on the rear surface of the <u>transfer</u> sheet by pressure <u>transfer</u> from the copy sheet. The heat transferable mirror image then can be applied to a T-shirt or other article by heat transfer.

#### Summary of Invention Paragraph (6):

[0005] The creation of personalized, creative designs or images on a fabric such as a T-shirt or the like through the use of a personal computer system has been described. The method involves electronically generating an image, electronically transferring the image to a printer, printing the image with the aid of the printer on an obverse surface of a transfer sheet which has a final or top coating consisting essentially of Singapore Dammar Resin, positioning the obverse face of the transfer sheet against the fabric, and applying energy to the rear of the transfer sheet to transfer the image to the fabric. The transfer sheet can be any commercially available transfer sheet, the heat-transferable coating of which has been coated with an overcoating of Singapore Dammar Resin. The use of abrasive particles in the Singapore Dammar Resin coating also has been described. The abrasive particles serve to enhance the receptivity of the transfer sheet to various inks and wax-based crayons.

### Summary of Invention Paragraph (7):

[0006] Additionally, improved heat <u>transfer</u> papers having an enhanced receptivity for images made by wax-based crayons, thermal printer ribbons, and impact ribbon or dot-matrix printers have been disclosed. For example, a cellulosic base sheet has an image-receptive coating containing from about 15 to about 80 percent of a film-forming binder and from about 85 to about 20 percent by weight of a powdered polymer consisting of particles having diameters from about 2 to about 50 micrometers. The binder typically is a latex. Alternatively, a cellulosic base sheet has an image-receptive coating which typically is formed by melt extrusion or by laminating a film to the base sheet. The surface of the coating or film then is roughened by, for example, passing the coated base sheet through an embossing roll.

#### Summary of Invention Paragraph (8):

[0007] Some effort also has been directed at generally improving the <u>transfer</u> of an image-bearing laminate to a substrate. For example, an improved release has been described, in which upon <u>transfer</u> the release splits from a carrier and forms a protective coating over the transferred image. The release is applied as a solution and contains a montan wax, a rosin ester or hydrocarbon resin, a solvent, and an ethylene-vinyl acetate copolymer having a low vinyl acetate content.

## Summary of Invention Paragraph (9):

[0008] Additional effort has been directed to improving the adhesion of the transferred laminate to porous, semi-porous, or non-porous materials, and the development of a conformable <u>transfer</u> layer which enables the melt <u>transfer</u> web to be used to transfer images to uneven surfaces.

## Summary of Invention Paragraph (10):

[0009] It is well known by those having ordinary skill in the art that current ink jet inks are aqueous-based systems. That is, the dyes employed in such inks are soluble in water. Thus, substrates printed with ink jet inks have a pronounced proclivity to run or even lose an image in the presence of moisture or water. Moreover, customer-selected graphics produced by desk-top publishing software and printed by ink jet printers result in graphics which in general are not transferred satisfactorily by known heat transfer papers. This is particularly true when transfer is attempted with a hand-held iron. Consequently, there is an opportunity for an improved heat transfer paper which has been developed specifically for graphics printed with an ink jet printer, i.e., an ink-jet printable heat transfer paper. There also is an opportunity for an improved heat transfer paper which has improved durability, especially in the presence of water, and which results in a softer, more pliable transferred image. More generally, there is an opportunity for an improved material which has been developed specifically for graphics printed with an ink jet printer, wherein the printed graphics will have improved durability, especially in the presence of water.

## Summary of Invention Paragraph (16):

[0014] The present invention also provides an ink jet printable material which includes a flexible first layer having first and second surfaces and a second layer. The first layer may be a film or a fibrous sheet-like material as described above. The second layer overlays and is bonded to the first surface of the first layer as described above, and includes a nonwoven web formed from a natural or synthetic polymer, again as described above. The second layer contains from about 0.1 to about 20 percent by weight, based on the weight of the polymer of which the second layer is composed, of a material which increases the viscosity of an ink jet ink when printed on the second layer. Such material may be, by way of illustration only, a poly(vinyl alcohol) or a polyoxyethylene. The second layer also may contain from about 0.1 to about 5 percent by weight, again based on the weight of the of the polymer of which the second layer is composed, of a cationic polymer.

#### Summary of Invention Paragraph (17):

[0015] The present invention further provides an <u>ink jet</u> printable heat <u>transfer</u> material which includes a flexible first layer having first and second surfaces and a second layer as already described. The first layer may be a film or a fibrous sheet-like material. For example, the fibrous sheet-like material may be a cellulosic nonwoven web. As another example, the first layer may be a latex-impregnated paper.

## Summary of Invention Paragraph (18):

[0016] The second layer overlays and is bonded to the first surface of the first layer and includes a nonwoven web formed from a thermoplastic polymer. For example, the second layer may be a meltblown web formed from, by way of example only, a polyamide. The first layer may have a basis weight of from about 20 to about 140 gsm. The thermoplastic polymer may have a melting point of from about 90.degree. C. to about 250.degree. C. and the second layer may have a basis weight of at least about 10 gsm. For example, the second layer may have a basis weight of from about 10 gsm to about 115 gsm. As another example, the second layer may have a basis weight of from about 17 gsm to about 115 gsm.

#### Summary of Invention Paragraph (21):

[0019] The second layer contains from about 0.1 to about 20 percent by weight, based on the weight of the polymer of which the second layer is composed, of a material which increases the viscosity of an ink jet ink when printed on the second layer. Such material may be, by way of illustration only, a poly(vinyl alcohol) or a polyoxyethylene. The second layer also may contain from about 0.1 to about 5 percent by weight, based on the weight of the polymer of which the second layer is composed, of a cationic polymer. For example, the cationic polymer may be a polyamide with cationic functional groups, an amide-epichlorohydrin resin, a polyethyleneimine, a polyacrylamide with cationic functional groups, or an urea-formaldehyde resin. Further, the second layer may contain, in amounts from about 0.1 to about 80 percent by weight of the polymer mass being transferred, a binder which functions as a meltable polymer adhesive (referred to as such hereinafter) which becomes part of the garment. For example, the meltable polymer adhesive may be an ethylene-acrylic acid copolymer, a vinyl chloride-acrylic acid copolymer, a polyacrylate, or a phenoxy resin.

## Summary of Invention Paragraph (22):

[0020] The present invention additionally provides a method of preparing a printable material which involves providing a flexible first layer having first and second surfaces, the flexible first layer being a film or a cellulosic nonwoven web; providing a second layer which includes a nonwoven web formed from a natural or synthetic polymer; overlaying the second layer on the first surface of the first layer. If the material is to be printed on with an <a href="ink jet">ink jet</a> printer, the method may further include treating the second layer with a composition which includes water and a material which increases the viscosity of an <a href="ink jet">ink jet</a> ink when printed on the second layer. Such material may be, by way of illustration only, a poly(vinyl alcohol) or a polyoxyethylene. Treating is carried out under conditions sufficient to provide an amount of the material in the second layer of from about 0.1 to about 20 percent by weight, on a dry weight basis, based on the weight of the second layer before treatment (i.e., based on the weight of the polymer of which the second layer is

composed). The second layer also may be treated with a solution of a cationic polymer under conditions sufficient to provide an amount of cationic polymer in the second layer of from about 0.1 to about 5 percent by weight, again based on the weight of the second layer before treatment. The second layer may be treated sequentially with two different compositions containing the <a href="ink jet">ink jet</a> ink viscosity increasing material and the cationic polymer, respectively, or with a single composition containing both the <a href="ink jet">ink viscosity increasing material and the cationic polymer. The first and second layers are as already defined.

## Summary of Invention Paragraph (23):

[0021] The present invention also provides a method of preparing a printable material which involves providing a flexible first layer having first and second surfaces, the flexible first layer being a film or a cellulosic nonwoven web; providing a second layer which includes a nonwoven web formed from a natural or synthetic polymer; coating the first surface of the first layer with an adhesive; and overlaying the second layer on the adhesive coating to bond the second layer to the first layer. As with the preceding method, if the material is to be printed on with an ink jet printer, the method may further include treating the second layer with a composition which includes water and a material which increases the viscosity of an ink jet ink when printed on the second layer. Again, such material may be, by way of illustration only, a poly(vinyl alcohol) or a polyoxyethylene and treating is carried out under conditions sufficient to provide an amount of the material in the second layer of from about 0.1 to about 20 percent by weight, on a dry weight basis, based on the weight of the second layer before treatment. The second layer also may be treated with a solution of a cationic polymer under conditions sufficient to provide an amount of cationic polymer in the second layer of from about 0.1 to about 5 percent by weight, based on the weight of the second layer before treatment. The second layer may be treated sequentially with two different compositions containing the ink jet ink viscosity increasing material and the cationic polymer, respectively, or with a single composition containing both the ink jet ink viscosity increasing material and the cationic polymer. The first and second layers are as already defined.

#### Summary of Invention Paragraph (24):

[0022] In any of the foregoing methods, the use of a second layer prepared from a thermoplastic polymer permits the resulting material to be employed as a heat transfer material. This is particularly true where the thermoplastic polymer has a melting point of from about 90.degree. C. to about 250.degree. C. Where the resulting material is to be employed as a heat transfer material, any of the foregoing methods may further include treating the second layer with an aqueous dispersion of a meltable polymer adhesive which becomes part of the garment. Such treatment is carried out under conditions sufficient to provide an amount of the meltable polymer adhesive in the second layer which is from about 0.1 to about 80 percent by weight of the polymer mass being transferred. Treatment may be separate from or simultaneous with any or all other treatments required by any given method. For example, where treatments with a material which increases the viscosity of an ink jet ink when printed on the second layer, a cationic polymer, and a meltable polymer adhesive are required, three different treating solutions or compositions may be employed. As another example, two treating solutions or compositions may be utilized, with any two of the three materials being present in the same treating solution composition. As still another example, all three materials may be present in a single treating composition. Any given treating solution or composition may be applied by any method known to those having ordinary skill in the art, including those methods already indicated. Moreover, the same method may be employed for each treating solution or composition, or as many different methods as there are different treating solutions or compositions may be utilized.

#### Summary of Invention Paragraph (25):

[0023] The present invention further provides a method of preparing a material having durable graphic printed thereon which involves providing a flexible first layer having first and second surfaces, the flexible first layer being a film or a cellulosic nonwoven web; providing a second layer which includes a nonwoven web formed from a thermoplastic polymer; overlaying the second layer on the first surface of the first layer; bonding the second layer to the first surface of the first layer; printing an image on the treated second layer; and fusing the second layer. The first and second layers are as already defined. If the material is to be printed on with an ink jet

printer, the method may further include treating the second layer with a composition which includes water and a material which increases the viscosity of an ink jet ink when printed on the second layer.

## Summary of Invention Paragraph (27):

[0025] The present invention still further provides a method of preparing a material having durable graphics thereon which involves providing a printable material having a first layer and a second layer; printing an image on the second layer; and fusing the second layer. The printable material includes a flexible first layer having first and second surfaces, the flexible first layer being a film or a cellulosic nonwoven web and having a basis weight of from about 20 to about 140 grams per square meter; and a second layer which comprises a nonwoven web formed from a thermoplastic polymer, which second layer overlays and is bonded to the first surface of the first layer, has a melting point of from about 90.degree. C. to about 250.degree. C., and has a basis weight of at least about 10 gsm. The second layer may include from about 0.1 to about 20 percent by weight, on a dry weight basis, based on the weight of the second layer, of a material which increases the viscosity of an ink jet ink when printed on the second layer. The method also may include transferring the fused second layer to a fabric under the influence of heat and pressure.

## Summary of Invention Paragraph (32):

[0029] The term "thermoplastic polymer" is used herein to mean any polymer which softens and flows when heated; such a polymer may be heated and softened a number of times without suffering any basic alteration in characteristics, provided heating is below the decomposition temperature of the polymer. Examples of thermoplastic polymers include, by way of illustration only, end-capped polyacetals, such as poly(oxymethylene) or polyformaidehyde, poly(trichloroacetaldehyde), poly(n-valeraldehyde), poly(acetaldehyde), and poly(propionaldehyde); acrylic polymers, such as polyacrylamide, poly(acrylic acid), poly(methacrylic acid), poly(ethyl acrylate), and poly(methyl methacrylate); fluorocarbon polymers, such as poly(tetrafluoroethylene), perfluorinated ethylene-propylene copolymers, ethylene-tetrafluoroethylene copolymers, poly(chlorotrifluoroethylene), ethylene-chlorotrifluoroethylene copolymers, poly(vinylidene fluoride), and poly(vinyl fluoride); polyamides, such as poly(6-aminocaproic acid) or poly(e-caprolactam)), poly(hexamethylene adipamide), poly(hexamethylene sebacamide), and poly(11-aminoundecanoic acid); polyaramides, such as poly(imino-1,3-phenyleneiminoisophthaloy1) or poly(m-phenylene isophthalamide); parylenes, such as poly-p-xylylene and poly(chloro-p-xylylene); polyaryl ethers, such as poly(oxy-2,6-dimethyl-1-,4-phenylene) or poly(p-phenylene oxide); polyaryl sulfones, such as poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene-isopropylidene-1,4-phenylene) and poly(sulfonyl-1,4-phenyleneoxy-1,4-phenylenesulfony-1-4,4'-biphenylene); polycarbonates, such as poly(bisphenol A) or poly(carbonyidioxy-1,4-phenyleneisopropylidene-1,4-phenylene); polyesters, such as poly(ethylene terephthalate), poly(tetramethylene terephthalate), and poly-(cyclohexylene-1,4-dimethylene terephthalate) or poly(oxymethylene-1,4-cyclohexylenemethyleneoxyterephthaloyl); polyaryl sulfides, such as poly(p-phenylene sulfide) or poly(thio-1,4-phenylene); polyimides, such as poly(pyromellitimido-1,4-phenylene); polyolefins, such as polyethylene, polypropylene, poly(1-butene), poly(2-butene), poly(1-pentene), poly(2-pentene), poly(3-methyl-1-pentene), and poly(4-methyl-1-pentene); vinyl polymers, such as poly(vinyl acetate), poly(vinylidene chloride), and poly(vinyl chloride); diene polymers, such as 1,2-poly-1,3-butadiene, 1,4-poly-1,3-butadiene, polyisoprene, and polychloroprene; polystyrenes; copolymers of the foregoing, such as acrylonitrile-butadiene-styrene (ABS) copolymers; and the like.

#### Summary of Invention Paragraph (40):

[0037] The term "material which increases the viscosity of an ink jet ink when printed on the second layer" is intended to include any material which acts as an ink jet ink viscosity modifier as described herein. For example, such material may be, by way of illustration only, a poly(vinyl alcohol) or a polyoxyethylene or poly(ethylene glycol). When a poly(ethylene glycol) is employed, it desirably will be a poly(ethylene glycol) having a weight-average molecular weight of from about 100,000 to about 2,000,000. The poly(ethylene glycol) desirably will have a weight-average molecular weight of from about 100,000 to about 600,000.

## Summary of Invention Paragraph (41):

[0038] As noted above, the ink jet printable material of the present invention includes a flexible first layer having first and second surfaces and a second layer. The first layer may be a film or a fibrous sheet-like material. For example, the first layer may be a cellulosic nonwoven web. As another example, the first layer may be a latex-impregnated paper.

#### Summary of Invention Paragraph (45):

[0042] The second layer may contain from about 0.1 to about 20 percent by weight, based on the weight of the second layer, of a material which increases the viscosity of an ink jet ink when printed on the second layer. Such material may be, by way of illustration only, a poly(vinyl alcohol) or a polyoxyethylene. Such material may be, by way of illustration only, a poly(vinyl alcohol) or a polyoxyethylene. It may be applied by any convenient means to the second layer. For example, the material may be dissolved in a suitable solvent, such as water, and applied to the second layer by Meyer rod, doctor blade, spraying, dipping and nipping, gravure printing, or other known method.

#### Summary of Invention Paragraph (46):

[0043] The second layer also may contain from about 0.1 to about 5 percent by weight, based on the weight of the second layer, of a cationic polymer. Examples of cationic polymers include, by way of illustration only, polyamides, amide-epichlorohydrin resins, polyethyleneimines, polyacrylamides, and urea-formaldehyde resins. As with the ink viscosity-reducing material, the cationic polymer may be dissolved in a suitable solvent, such as water, and applied in a similar manner. If desired, both the ink viscosity-reducing material and the cationic polymer may be present in the same solution.

## <u>Summary of Invention Paragraph</u> (47):

[0044] The present invention further provides an <u>ink jet</u> printable heat <u>transfer</u> material which includes a flexible first layer having first and second surfaces and a second layer. The first layer may be a film or a fibrous sheet-like material. For example, the fibrous sheet-like material may be a cellulosic nonwoven web. As another example, the first layer may be a latex-impregnated paper.

## Summary of Invention Paragraph (48):

[0045] The second layer overlays and is bonded to the first surface of the first layer and includes a nonwoven web formed from a thermoplastic polymer. For example, the second layer may be a meltblown web formed from, by way of example only, a polyamide. The first layer may have a basis weight of from about 20 to about 140 gsm. The thermoplastic polymer may have a melting point of from about 90.degree. C. to about 250.degree. C. and the second layer may have a basis weight of at least about 10 gsm. For example, the second layer may have a basis weight of from about 10 gsm to about 115 gsm. As another example, the second layer may have a basis weight of from about 17 gsm to about 115 gsm.

#### Summary of Invention Paragraph (51):

[0048] The second layer may contain from about 0.1 to about 20 percent by weight, based on the weight of the second layer, of a material which increases the viscosity of an ink jet ink when printed on the second layer. For example, the second layer may contain from about 0.1 to about 5 percent by weight of the ink viscosity-increasing material. Such material may be, by way of illustration only, a poly(vinyl alcohol) or a polyoxyethylene. It may be applied by any convenient means to the second layer. For example, the material may be dissolved in a suitable solvent, such as water, and applied to the second layer by Meyer rod, doctor blade, spraying, dipping and nipping, gravure printing, or other known method. The second layer also may contain from about 0.1 to about 5 percent by weight, based on the weight of the second layer, of a cationic polymer. The cationic polymer may be applied as a solution in a like manner.

## Summary of Invention Paragraph (54):

[0051] In general, any of the fillers and pigments typically present in a papermaking furnish may be included with the meltable polymer adhesive. Examples of such fillers and pigments include, by way of illustration only clay, talc, silica, titanium dioxide; and colored pigments. Fillers and pigments may be present in the second layer

at levels of from about 0.1 to about 40 percent by weight, based on the amount of the meltable polymer adhesive on a dry weight basis. Where the printable material is to be employed as a heat transfer material, the amount of fillers and pigments present in the second layer may vary from about 0.1 to about 5 percent by weight.

## Summary of Invention Paragraph (55):

[0052] Finally, particles of thermoplastic polymers also may be present in the second layer. In general, the powdered thermoplastic polymer can be any thermoplastic polymer which meets the criteria set forth herein. For example, the powdered thermoplastic polymer may be a polyolefin, polyester, polyamide, or an ethylene-vinyl acetate copolymers. Such particles may be present in the second layer at levels of from about 0.1 to about 40 percent by weight, based on the amount of the meltable polymer adhesive on a dry weight basis. Where the printable material is to be employed as a heat transfer material, the amount of thermoplastic particles present in the second layer may vary from about 0.1 to about 5 percent by weight.

## Summary of Invention Paragraph (56):

[0053] Thus, the heat transfer material of the present invention is a nonwoven web laminated to a flexible substrate. A small amount of an additive, desirably from about 0.1 to about 5 percent, based on the weight of the nonwoven web, is added to prevent ink spreading or feathering. This additive is the viscosity increasing material already described. Also as already described, the material may be applied to the nonwoven web as, for example, a water solution, and then dried. Poly(vinyl alcohol) and polyoxyethylene or poly(ethylene oxide) have been shown to be very effective at low add-ons. This is probably due to their ability to provide high viscosity to the inks very rapidly before spreading can occur.

## Summary of Invention Paragraph (57):

[0054] Advantages of the <u>ink jet</u> printable material of the present invention include the wide availability of polymers for meltblown webs, ease of constructing a heavy, absorbent coating, and ease of fabricating a laminate. The resulting product appears to give less print feathering and, with the proper polymer selection, provides a heat <u>transfer</u> material which imparts good washability of fabrics to which images were transferred by means of the heat <u>transfer</u> material of the present invention. Also, it is possible to use the concept to produce fusible <u>ink jet</u> printable, durable coatings. Yarns possibly may be made by slitting and twisting the meltblown webs.

## Summary of Invention Paragraph (58):

[0055] The ink jet printable heat transfer material of the present invention may contain, in amounts from zero to about 80 percent by weight of the polymer mass being transferred, a meltable polymer adhesive which becomes part of the garment. By way of illustration, the meltable polymer adhesive may be present in an amount of from about 0.1 to about 80 percent by weight. For example, the meltable polymer adhesive may be an ethylene-acrylic acid copolymer, a vinyl chloride-acrylic acid copolymer, a polyacrylate, or a phenoxy resin. The total weight of the transferable polymer mass typically is from about 25 to about 70 gsm. Thus far, heat transfer materials having a high proportion of meltblown polymer (i.e., relatively low amounts of meltable adhesive) have been most effective. The heavier meltblown webs provide more surface area for rapid ink absorption, and the presence of polymer in higher proportions provides better ink retention (better washability of the transferred image). With pigmented ink jet inks or with other pigmented printing methods, it is expected that polymer types other than the polyamides employed in the examples would provide acceptable washability as well.

#### Summary of Invention Paragraph (59):

[0056] As already stated, the heat <u>transfer</u> material may have a release coat or layer, whether or not an adhesive layer is employed for bonding the second layer to the first layer. A release layer is desirable for transferring images by means of a hand-held iron or if cold release properties are desired.

## Summary of Invention Paragraph (60):

[0057] The present invention additionally provides a method of preparing a printable material which involves providing a flexible first layer having first and second surfaces, the flexible first layer being a film or a cellulosic nonwoven web; providing a second layer which includes a nonwoven web formed from a natural or

synthetic polymer; overlaying the second layer on the first surface of the first layer; and bonding the second layer to the first surface of the first layer. If the material is to be printed on with an ink jet printer, the method may further include treating the second layer with a composition which includes water and a material which increases the viscosity of an ink jet ink when printed on the second layer. Such material may be, by way of illustration only, a poly(vinyl alcohol) or a polyoxyethylene. Treating is carried out under conditions sufficient to provide an amount of the material in the second layer of from about 0.1 to about 20 percent by weight, on a dry weight basis, based on the weight of the second layer before treatment (i.e., based on the weight of the polymer of which the second layer is composed). The second layer also may be treated with a solution of a cationic polymer under conditions sufficient to provide an amount of cationic polymer in the second layer of from about 0.1 to about 5 percent by weight, again based on the weight of the second layer before treatment. The second layer may be treated sequentially with two different compositions containing the ink jet ink viscosity increasing material and the cationic polymer, respectively, or with a single composition containing both the ink jet ink viscosity increasing material and the cationic polymer. The first and second layers are as already defined.

## Summary of Invention Paragraph (61):

[0058] The present invention also provides a method of preparing a printable material which involves providing a flexible first layer having first and second surfaces, the flexible first layer being a film or a cellulosic nonwoven web; providing a second layer which includes a nonwoven web formed from a natural or synthetic polymer; coating the first surface of the first layer with an adhesive; and overlaying the second layer on the adhesive coating to bond the second layer to the first layer. As with the preceding method, if the material is to be printed on with an ink jet printer, the method may further include treating the second layer with a composition which includes water and a material which increases the viscosity of an ink jet ink when printed on the second layer. Again, such material may be, by way of illustration only, a poly(vinyl alcohol) or a polyoxyethylene and treating is carried out under conditions sufficient to provide an amount of the material in the second layer of from about 0.1 to about 20 percent by weight, on a dry weight basis, based on the weight of the second layer before treatment. The second layer also may be treated with a solution of a cationic polymer under conditions sufficient to provide an amount of cationic polymer in the second layer of from about 0.1 to about 5 percent by weight, based on the weight of the second layer before treatment. The second layer may be treated sequentially with two different compositions containing the ink jet ink viscosity increasing material and the cationic polymer, respectively, or with a single composition containing both the ink jet ink viscosity increasing material and the cationic polymer. The first and second layers are as already defined.

#### Summary of Invention Paragraph (62):

[0059] In any of the foregoing methods, the use of a second layer prepared from a thermoplastic polymer permits the resulting material to be employed as a heat transfer material. This is particularly true where the thermoplastic polymer has a melting point of from about 90.degree. C. to about 250.degree. C. Where the resulting material is to be employed as a heat transfer material, any of the foregoing methods may further include treating the second layer with an aqueous dispersion of a meltable ' polymer adhesive which becomes part of the garment. Such treatment is carried out under conditions sufficient to provide an amount of the meltable polymer adhesive in the second layer which is from about 0.1 to about 80 percent by weight of the polymer mass being transferred. Treatment may be separate from or simultaneous with any or all other treatments required by any given method. For example, where treatments with a material which increases the viscosity of an ink jet ink when printed on the second layer, a cationic polymer, and a meltable polymer adhesive are required, three different treating solutions or compositions may be employed. As another example, two treating solutions or compositions may be utilized, with any two of the three materials being present in the same treating solution composition. As still another example, all three materials may be present in a single treating composition. Any given treating solution or composition may be applied by any method known to those having ordinary skill in the art, including those methods already indicated. Moreover, the same method may be employed for each treating solution or composition, or as many different methods as there are different treating solutions or compositions may be utilized.

## Summary of Invention Paragraph (63): .

[0060] The present invention further provides a method of preparing a material having durable graphic printed thereon which involves providing a flexible first layer having first and second surfaces, the flexible first layer being a film or a cellulosic nonwoven web; providing a second layer which includes a nonwoven web formed from a thermoplastic polymer; overlaying the second layer on the first surface of the first layer; bonding the second layer to the first surface of the first layer; printing an image on the treated second layer; and fusing the second layer. The first and second layers are as already defined. If the material is to be printed on with an ink jet printer, the method may further include treating the second layer with a composition which includes water and a material which increases the viscosity of an ink jet ink when printed on the second layer.

#### Summary of Invention Paragraph (65):

[0062] The present invention still further provides a method of preparing a material having durable graphics thereon which involves providing a printable material having a first layer and a second layer; printing an image on the second layer; and fusing the second layer. The printable material includes a flexible first layer having first and second surfaces, the flexible first layer being a film or a cellulosic nonwoven web and having a basis weight of from about 20 to about 140 grams per square meter; and a second layer which comprises a nonwoven web formed from a thermoplastic polymer, which second layer overlays and is bonded to the first surface of the first layer, has a melting point of from about 90 degree. C. to about 250 degree. C., and has a basis weight of at least about 10 gsm. The second layer may include from about 0.1 to about 20 percent by weight, on a dry weight basis, based on the weight of the second layer, of a material which increases the viscosity of an ink jet ink when printed on the second layer. The method also may include transferring the fused second layer to a fabric under the influence of heat and pressure.

#### Detail Description Paragraph (2):

[0064] The examples all utilized meltblown webs prepared with a copolyamide having a melting point of 115.degree. C. (Platamid.RTM. H585, Elf Atochem North America, Inc., Philadelphia, Pa.). Meltblown webs having basis weights of 12.5, 18, 36, and 54 gsm were prepared. The meltblown copolyamide fibers were very slow to harden, resulting in a blocked roll. The material was, however, successfully wound onto release paper. After hardening, the resulting webs were strongly bonded and very porous. Unlike webs of faster hardening polymers such as polypropylene, the webs were somewhat film-like and it was difficult to abrade fibers from them. This very surprising result gave a laminate which behaves almost like a coated paper without any need for further bonding or other densification. Print tests were done with a Canon BJC 600 ink jet printer.

#### Detail Description Paragraph (13):

[0075] Treatment weights were calculated from a wet coating weight since the treatment weights were quite small compared to the total laminate weight. Transfers were done to 100 percent cotton T-shirt material with a Hix T-shirt press (Hix Corp., Pittsburgh, Kans.) for 25 seconds at 350.degree. F. (177.degree. C.). Wash tests were done in a home washing machine on the warm/warm setting using Surf.RTM. detergent. Test results were compared to printing and transfers made with Type C-90642 heat transfer paper, a product which has gained acceptance in the market.

## Detail Description Paragraph (14):

[0076] Various heat transfer materials were prepared by pressing the meltblown webs onto a paper substrate using the T-shirt press at 160.degree. F. (71.degree. C.) for 25 seconds. The treatment solutions were applied to the meltblown webs with a No. 6 Meyer rod. The various materials are summarized in Table 2 and the printing and washing test results are summarized in Table 3.

## Detail Description Table CWU (2):

3TABLE 2 Summary of Heat Transfer Materials First Layer Second Layer Treatment Example Code Basis Weight.sup.a Weight.sup.a Solution 1 A 12.5 None None 2 A 18 None None 3 B 12.5 None None 4 A 18 1.6 A 5 A 18 0.8 B 6 B 18 0.8 C 7 B 18 0.8 D 8 C 36 1.2 D 9 C 36 2.4 E 10 C 36 3.2 F 11 C 36 3.2 G 12 C 36 3.2 H 13 C 36 3.2 I 14 C 36 3.2 J 15 C 36 3.2 K 16 C 36 3.2 L 17 C 36 0.8 M 18 C 54 1.6 A 19 C 71 1.6 A 20 C 71 0.8 B 21 C 71 None None 22 D 71 0.8 N 23 D 71 0.8 M 24 D 71 0.4 Q 25 D 71 0.4 Q 26 D 54 0.8 A 27 C

71 2.8 P .sup.aBasis weight in gsm.

#### CLAIMS:

- 6. An <u>ink jet</u> printable material comprising: a flexible first layer having first and second surfaces, the flexible first layer being a film or a cellulosic nonwoven web; and a second layer overlaying and bonded to the first surface of the first layer, which second layer comprises a nonwoven web formed from a natural or synthetic polymer; wherein: the first layer has a basis weight of from about 20 to about 140 grams per square meter; the second layer has a basis weight of at least about 10 grams per square meter; and the second layer contains from about 0.1 to about 20 percent by weight, based on the weight of the second layer, of a material which increases the viscosity of an <u>ink jet</u> ink when printed on the second layer.
- 7. The <u>ink jet</u> printable material of claim 6, in which the first layer is a cellulosic nonwoven web.
- 8. The <u>ink jet</u> printable material of claim 7, in which the cellulosic nonwoven web is a latex-impregnated paper.
- 9. The <u>ink jet</u> printable material of claim 6, in which the second layer is bonded to the first surface of the first layer by means of an adhesive.
- 10. The <u>ink jet</u> printable material of claim 9, in which the adhesive is a heat-activated ethylene-acrylic acid copolymer.
- 11. The <u>ink jet</u> printable material of claim 6, in which the second layer is thermally bonded to the first surface of the first layer.
- 12. The <u>ink jet</u> printable material of claim 6, in which the material which increases the viscosity of an <u>ink jet</u> ink when printed on the second layer is selected from the group consisting of poly(vinyl alcohol) and polyoxyethylene.
- 13. The <u>ink jet</u> printable material of claim 6, in which the second layer contains from about 0.1 to about 5 percent by weight, based on the weight of the second layer, of a cationic polymer.
- 14. An <u>ink jet</u> printable heat <u>transfer</u> material comprising: a flexible first layer having first and second surfaces, the flexible first layer being a film or a cellulosic nonwoven web; and a second layer overlaying and bonded to the first surface of the first layer, which second layer comprises a nonwoven web formed from a thermoplastic polymer; wherein: the first layer has a basis weight of from about 20 to about 140 grams per square meter; the thermoplastic polymer has a melting point of from about 90.degree. C. to about 250.degree. C.; the second layer has a basis weight of at least about 10 grams per square meter; and the second layer contains from about 0.1 to about 20 percent by weight, based on the weight of the second layer, of a material which increases the viscosity of an <u>ink jet</u> ink when printed on the second layer.
- 15. The ink jet printable heat transfer material of claim 14, in which the first layer is a cellulosic nonwoven web.
- 16. The  $\underline{ink\ jet}$  printable heat  $\underline{transfer}$  material of claim 15, in which the cellulosic nonwoven web is a latex-impregnated paper.
- 17. The  $\underline{ink}$  jet printable heat  $\underline{transfer}$  material of claim 14, in which the nonwoven web is a meltblown web.
- 18. The <u>ink jet</u> printable heat <u>transfer</u> material of claim 17, in which the thermoplastic polymer is a polyamide.
- 19. The <u>ink jet</u> printable heat <u>transfer</u> material of claim 18, in which the <u>polyamide</u> has a melting point of from about 90.degree. C. to about 160.degree. C.
- 20. The ink jet printable heat transfer material of claim 14, in which the second

layer is bonded to the first surface of the first layer by means of an adhesive.

- 21. The <u>ink jet</u> printable heat <u>transfer</u> material of claim 20, in which the adhesive is a heat-activated ethylene-acrylic acid copolymer.
- 22. The <u>ink jet</u> printable heat <u>transfer</u> material of claim 20, in which a release layer is present between the first layer and the adhesive.
- 23. The <u>ink jet</u> printable heat <u>transfer</u> material of claim 14, in which the second layer is thermally bonded to the first surface of the first layer.
- 24. The <u>ink jet</u> printable heat <u>transfer</u> material of claim 14, in which the material which increases the viscosity of an <u>ink jet</u> ink when printed on the second layer is selected from the group consisting of poly(vinyl alcohol) and polyoxyethylene.
- 25. The <u>ink jet</u> printable heat <u>transfer</u> material of claim 14, in which the second layer contains from about 0.1 to about 5 percent by weight, based on the weight of the second layer, of a cationic polymer.
- 26. The <u>ink jet</u> printable heat <u>transfer</u> material of claim 14, in which the second layer contains from about 0.1 to about 80 percent by weight, based on the polymer mass being transferred, of a meltable polymer adhesive.
- 28. The method of claim 27 which further comprises treating the second layer with a composition comprising water and a material which increases the viscosity of an <u>ink</u> <u>jet</u> ink when printed on the second layer, under conditions sufficient to provide in the second layer from about 0.1 to about 20 percent by weight, based on the weight of the second layer, of said material.
- 30. The method of claim 29 which further comprises treating the second layer with a composition comprising water and a material which increases the viscosity of an  $\underline{ink}$   $\underline{jet}$  ink when printed on the second layer, under conditions sufficient to provide in the second layer from about 0.1 to about 20 percent by weight, based on the weight of the second layer, of said material.
- 32. The method of claim 31 which further comprises treating the second layer, before printing an image thereon, with a composition comprising water and a material which increases the viscosity of an ink jet ink when printed on the second layer, under conditions sufficient to provide in the second layer from about 0.1 to about 20 percent by weight, based on the weight of the second layer, of said material.
- 33. The method of claim 32, in which the second layer further comprises from about 0.1 to about 20 percent by weight, based on the weight of the second layer, of a material which increases the viscosity of an ink jet ink when printed on the second layer.

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## overview

Features | Functions | Applications

Orgasol® Últrafine polyamide powders are a range of polymers and copolymers of lauryllactam (PA 12) and or caprolactam (PA 6) obtained by direct polymerization. Due to this unique process a range of Orgasol® powders with a unique spherical shape and very narrow particle size distribution are available. The grades differ in terms of particle size (from 5 to 60 microns), specific surface area and melting point.

The characteristics and properties of Orgasol® powders, extremely narrow particle size distribution, unique surface structure and morphology, contrast to other powders obtained from precipitation or ground processes.

#### Features:

Three Classes of Products:

- Polyamide 6
- Polyamide 12
- Polyamide 6/12 copolymers
- Ultra-fine Polyamide Powders
- Spherical shape particles
- Narrow particle size distribution
- Uniform particle sizes ranging from 5 to 60 microns (+/- 1 to 3 microns)
- Microporous, high surface area structure
- Range of melting temperatures (140 to 220 °C)
- Low density

## **Functions:**

Matting or Flattening Agent

Gloss control or low gloss

Texturing or Texturizing Agent

Surface modification for unique and uniform appearance

Soft feel effect

Abrasion / Rub

Resistance Agent

High level of abrasion resistance

Solid Lubricant Agent

Control of the coefficient of friction

Scratch/Scuff

Resistance Agent

Improve the scratch resistance

Carrier

High porosity gives high loading capacity

Slow release properties

Binder

Forms uniform coatings or matrix

Filler

Chemically inert Low specific gravity

Applications:

Coatings

Solvent based, water based, powder, UV and EB formulations

Compatible with a variety of surfaces (metal, plastic, wood, paper, rubber and

glass)

Applied using a variety of processes (roller, spray and coil coating)

Used in numerous markets such as hardwood flooring, coil-coating, kitchen cabinet, furniture, toys, automotive, aerospace, general industrial and TV/Stereo

appliances

Composites

Thermoplastic binder for glass or carbon fibers

Thermoplastic matrix for metal injection molding - magnet

Inks/Vamishes

Water-based or solvent-borne inks or OPV (over print varnishes)

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11/17/03

Polyamide Such a

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Non-thixotropic matting agent in UV varnishes

Paper Coatings

Printability improvements Anti-blocking properties

Sealants/Primers

Low density filler for high performance sealants or primers

Orgasol® Powders is a registered trademark of ATOFINA.

## **Corporate Profile**

ATOFINA Chemicals, Inc., <a href="www.AtofinaChemicals.com">www.AtofinaChemicals.com</a>, is headquartered at 2000 Market Street in Philadelphia, PA, 19103 and can be re 7000. ATOFINA Chemicals, Inc. employs 3,000 people and reported sales in 2002 of \$1.4 billion. ATOFINA Chemicals is part of ATOFIN. largest chemical company with 71,500 employees and sales in 2002 of \$18.2 billion. ATOFINA is the chemical branch of TOTAL (NYSE: 4th largest oil and gas company with 121,000 employees and sales in 2002 of \$97.6 billion.

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'A' ATOFINA



L3: Entry 140 of 144

File: USPT

Jul 17, 1990

DOCUMENT-IDENTIFIER: US 4941923 A TITLE: Water-insoluble black pigment

### Abstract Text (1):

A water-insoluble black pigment produced by reacting C. I. Solubilized Sulphur Black 1 with a salt-forming agent selected from the group consisting of inorganic acid salts of alkylamine, alkoxyalkylamine, alkanolamine, carboxyalkylamine, alkylcarboxamide, allylamine, amide of unsaturated carboxylic acid, cyclic amine, cycloalkylamine, oxacycloalkylamine, morpholine derivative, arylamine, aralkylamine, pyridine derivative, quinoline, phthalimide, DL-.alpha.-amino-.epsilon.-caprolactam and .epsilon.-aminocaprolactam, and ammonium salt of the formula (1): ##STR1## wherein A.sub.1, A.sub.2, A.sub.3 and A.sub.4 each represent an alkyl or phenyl group and X-represents an anionic group.

#### Abstract Text (2):

The water-insoluble black pigment is usable as a colorant for printing ink, <u>ink for jet</u> printers, dot printer ribbon, and melt-transfer type printer, a charge-regulator for toner used on electrostatic recording system, a laser marking agent, a colorant for resin, an infrared absorber and the like.

## Brief Summary Text (3):

Black pigments are used in quantities in various industrial fields. For example, they are used as a colorant for paint, printing ink, ink for recording materials such as ribbon for dot printers, melt transfer ink or ink for ink-jet printers, a colorant for a toner for electrostatic photography, an infrared absorber, a laser-marking agent and a charge regulator. The black pigments include inorganic and organic pigments such as carbon black, Nigrosine dyestuffs, metal complex dyestuffs and the like.

## Brief Summary Text (10):

The present invention provides water-insoluble black pigments produced by reacting C. I. Solubilized Sulphur Black 1 with a salt-forming agent selected from the group consisting of inorganic acid salts of alkylamine, alkoxyalkylamine, alkanolamine, carboxyalkylamine, alkylcarboxyamide, allylamine, amide of unsaturated carboxylic acid, cyclic amine, cycloalkylamine, oxacycloalkylamine, morpholine derivative, arylamine, aralkylamine, pyridine derivative, quinoline, phthalimide, DL-.alpha.-amino-.epsilon.-caprolactam and .epsilon.-aminocaprolactam, and ammonium salt of the formula (1) (hereinafter referred to as a salt-forming agent): ##STR2##

## Detailed Description Text (10):

Among the alkylamines, alkoxyalkylamines, alkanolamines, carboxyalkylamines, alkylcarboxamides, allylamines, amides of unsaturated carboxylic acid, cyclic amines, cycloalkylamines, oxacycloalkylamines, morpholine derivatives, arylamines, aralkylamine, pyridine derivatives, quinoline, phthalimide, DL-.alpha.-amino-68
-caprolactam, .epsilon.-aminocaprolactam and ammonium salts of the above formula (1), examples of the alkylamines, alkoxyalkylamines, alkanolamines, carboxyalkylamines, alkylcarboxamides, allylamines, amides of unsaturated carboxylic acid, cyclic amines, cycloalkylamines, oxacycloalkylamines, morpholine derivatives, arylamines, aralkylamines, pyridine derivatives and ammonium salts of the formula (1) include the following compounds.

## Detailed Description Text (36):

The water-insoluble black pigments of the present invention are usable for various purposes. Namely, they are usable as colorants for printing inks, inks for ink jet printers, inks for dot printer ribbons, inks for melt transfer printing, inks for infrared OCR, colorants or charge-regulators for toners for electrostatic recording,

laser marking agents, colorants for resins and infrared absorbers.

## Detailed Description Text (37):

For example, ink for melt transfer printing is prepared by dissolving a black pigment of the present invention and a wax having a low melting point such as a fatty acid amide in a solvent such as acetone. The ink thus prepared is applied to, for example, a polyester sheet and the sheet is heated to vaporize the solvent such as acetone, thus forming an ink layer. Thus a heat melt transfer sheet usable for the thermal transfer printing onto PPC paper or the like by printing with a thermal printing head or the like is prepared.

## Detailed Description Text (38):

A water-insoluble black pigment of the present invention is mixed by grinding with epoxy resin, bromoepoxy resin, phenolic novolac, 2-methylimidazole (hardener), flame retardant, releasing agent, silane coupling agent and silica powder with a mixing roll heated at 80.degree. C. for 10 min to form a sheet. The sheet is cooled and pulverized to give a resin molding powder. A lead frame provided with semiconductor elements is sealed with the resin molding powder thus obtained by means of a transfer press to form a satin-finished resin-sealed semiconductor device having a surface roughness of 12 .mu. (the molding conditions include a temperature of 175.degree. C., a time of 2 min, a transfer pressure of 90 kg/cm.sup.2 and postcure temperature and time of 175.degree. C. and 10 h, respectively). The obtained resin-sealed semi-conductor device is irradiated with carbon dioxide laser through a given mask to mark the surface of the semiconductor device. Thus a quite clear-marked device can be obtained.

## Detailed Description Text (64):

A solution of a polyamide resin in toluene was applied to a capacitor paper having the thickness of 10 .mu.m with a bar coater to form a layer having a thickness of 6 .mu.m, which was then dried to form an intermediate adhesive layer. Separately, 2 parts of the water-insoluble black pigment produced in Example 6, 2 parts of a fatty acid amide as the melting point depressant, 0.8 part of carbon black having a surface coated with a vinyl chloride/vinyl acetate copolymer and 25 parts of acetone were kneaded together by means of a ball mill for 24 h to give a dispersion, which was applied on the intermediate adhesive layer, followed by evaporation of acetone to thereby form an ink layer having a thickness of 20 .mu.m. The black pigment was quite compatible with the fatty acid amide and the vinyl chloride/vinyl acetate copolymer. The ink sheet thus prepared was used for the transfer recording onto PPC paper with a thermal facsimile terminal. The conditions were: 0.4 W for each dot of the printing head, print heating time of 4 ms and, therefore, printing energy density of 40 mj/mm.sup.2. The recording was conducted repeatedly with the facsimile terminal using the same portion of the ink sheet while the recording paper was moved to have a new line each time under the above-described conditions. A print of a high density could be obtained. Even after repeating the printing 10 times, a sufficiently readable, clear print could be obtained. Even when the pattern of the characters was changed during the printing, the density of the transferred print was even. In the microscopic observation of the surface of the ink layer, it was found that the surface was flat and smooth. Even when the surface of the record was rubbed with fingers, the fingers were not stained and no dragging mark of the transferred image was observed.

## Detailed Description Text (65):

A molding epoxy resin composition comprising the components shown above was prepared as follows: the flame retardant and the inorganic filler were treated with the silane coupling agent. The other components were added thereto, pulverized and mixed together. The mixture was treated with a mixing roll heated at 80.degree. C. for 10 min to form a sheet, which was cooled and pulverized to form a resin powder. A lead frame provided with semiconductor elements was sealed with the molding powder by means of a transfer press to form a satin-finished resin-sealed semiconductor device having a surface roughness of 20 .mu. (the molding conditions included a temperature of 175.degree. C., a time of 2 h, a transfer pressure of 90 kg/cm.sup.2 and postcure temperature and time of 175.degree. C., and 10 h, respectively). The obtained resin-sealed semiconductor device was irradiated with a carbon dioxide gas laser (902 Laser Mark of Shibuya Koei Co., Ltd. having a maximum energy density of 0.4 Joule/cm.sup.2) through a given mask for 1/1,000,000 sec to mark the surface of the semiconductor. Thus a quite clear marking was obtained. It was thus confirmed that the

water-insoluble black pigment produced in Example 4 served as an excellent laser marking agent.

Detailed Description Paragraph Table (1):
Example No. Amine used
Example 7 H.sub.2 NCH.sub.3 Example 8 H.sub.2
NCH.sub.2 CH.sub.3 Example 9 H.sub.2 N(CH.sub.2).sub.11 CH.sub.3 Example 10
H.sub.2 NC.sub.18 H.sub.37 Example 11 H.sub.2 NC.sub.2 H.sub.4 OH Example 12
HN(C.sub.2 H.sub.4 OH).sub.2 Example 13 CH.sub.3 OCH.sub.2 CH.sub.2 CH.sub.2 NH.sub.2
Example 14 C.sub.9 H.sub.19 OCH.sub.2 CH.sub.2 CH.sub.2 NH.sub.2 Example 15 Morpholin
Example 16 Aniline Example 17 H.sub.2 NCOOC.sub.2 H.sub.5 Example 18 Acrylamide
polymer (MW:700,000 to 1,000,000) Example 19 DLalphaaminoepsilon. <u>-caprolactam</u>

#### CLAIMS:

1. A water-insoluble black pigment produced by reacting C. I. Solubilized Sulphur Black 1 with a salt-forming agent selected from the group consisting of inorganic acid salts of alkylamine, alkoxyalkylamine, alkanolamine, carboxyalkylamine, alkylcarboxamide, allylamine, amide of unsaturated carboxylic acid, cyclic amine, cycloalkylamine, oxacycloalkylamine, morpholine derivative, arylamine, aralkylamine, pyridine derivative, quinoline, phthalimide, DL-.alpha.-amino-.epsilon.-caprolactam and .epsilon.-aminocaprolactam, and ammonium salt of the formula (1): ##STR17## wherein A.sub.1, A.sub.2, A.sub.3 and A.sub.4 each represent an alkyl or phenyl group and X.sup.- represents an anionic group.